

Structure, stability and electronic properties of tricycle type graphane

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We propose a new allotrope of graphane, named as tricycle graphane, with a 4up/2down UUUDUD hydrogenation in each hexagonal carbon ring, which is different from previously proposed allotropes with UUDUUD (boat-1) and UUUUDD (boat-2) types of hydrogenation. Its stability and electronic structures are systematically studied using first-principles method. We find that the tricycle graphane is a stable phase in between the previously proposed chair and stirrup allotropes. Its electronic properties are very similar to those of chair, stirrup, boat-1, boat-2, and twist-boat allotropes. The negative Gibbs free energy of tricycle graphane is -91 meV/atom, which very close to that of the most stable chair one (-103 meV/atom). Thus, this new two-dimensional hydrocarbon may be produced in the process of graphene hydrogenation with a relative high probability compared to other conformers.

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INTRODUCTION

Graphene, a single layer of graphite, is the thinnest two-dimensional (2D) carbon material consisting of a monolayer carbon atoms in a honeycomb lattice. This novel material was experimentally discovered in 2004 [1] and has given rise to enormous scientific and technological impacts in relevant areas of physics, chemistry and materials sciences. It is considered as a revolutionary material for future generation of high-speed electronics, sensors, transparent electrodes due to its unusual electronic, optical and magnetic properties. For the purpose of modifying graphene for applications in future nano-electronics, many modified graphene-based materials, such as the graphene nanoribbons (GNRs) [2–4] and hydrogenated-graphene (graphane) [5–12], have been proposed and widely investigated.

Graphane, a 2D hydrocarbon material, was suggested first by Sluiter and Kawazoe [5] and synthesized [7] in 2009 through exposure of a single-layer graphene to a hydrogen plasma. Since then, many new configurations with low energies for this 2D hydrocarbon were proposed. The most stable configuration of graphane is named as "chair" [5, 6] with the UDUDUD hydrogenation in each hexagonal carbon ring as shown in Fig. 1 (a) (here we adopt the nomenclature in reference [11]). The second stable configuration named as "stirrup" [5, 9, 10] with the UUUDDD hydrogenation in each carbon ring is shown in Fig. 1 (a), whose energy is about 28 meV/atom larger than that of the chair one. From the point of view of stability, the following configurations for graphane allotropes are boat-1 [5, 6, 9] with the UUDUUU hydrogenation, boat-2 [9, 11] with the UUUUDD hydrogenation, twist-boat [12] with the UUDUDD hydrogenation and other configurations with relatively high energies reported in reference [8, 11]. The hydrogenation patterns of all above graphane allotropes can be divided in to

two groups: 3up/3down and 4up/2down. Interestingly, we notice that the hexagonal hydrocarbon rings in the most stable five graphane allotropes, namely chair, stirrup, boat-1, boat-2 and twist-boat, are equivalent. As mentioned in reference [11], there are many situations to hydrogenate a single six-carbon ring, such as 6U: UUUUUU; 5U: UUUUUD; 4U: UUUUDD, UUUDUD, and UUDUUD; 3U: UDUDUD, UUDUDD, and UUUDDD, 2U=4U, etc. In present work, with the restrictive condition of keeping the hexagonal hydrocarbon rings equivalent in the systems, we propose a tricycle graphane allotrope where each hexagonal hydrocarbon rings with the same UUUDUD hydrogenation are equivalent. This new graphane holds remarkable stability comparable to the most stable chair one, becoming the second stable graphane allotrope.

MODELS AND METHODS

To hydrogenate a six-carbon ring, there are finite situations (6U: UUUUUU; 5U: UUUUUD; 4U: UUUUDD, UUUDUD, UUDUUD; 3U: UDUDUD, UUDUDD, UUUDDD; 2U=4U, etc) according to mathematical permutation and combination principle. However, there are enormous situations for hydrogenated graphene because there are considerable patterns of the border between hexagonal carbon rings. Moreover, each carbon atom in graphene belongs to three neighboring hexagonal carbon rings and its hydrogenated configuration (up/down) will be counted into the hydrogenation situations of its three neighboring six-carbon rings, making the situation very complicated. However, we realize that the hexagonal hydrocarbon rings of the five most stable graphane allotropes, including chair, stirrup, boat-1, boat-2 and twist-boat configurations, are equivalent in each system, as shown in Fig.1. Under the restrictive condition of

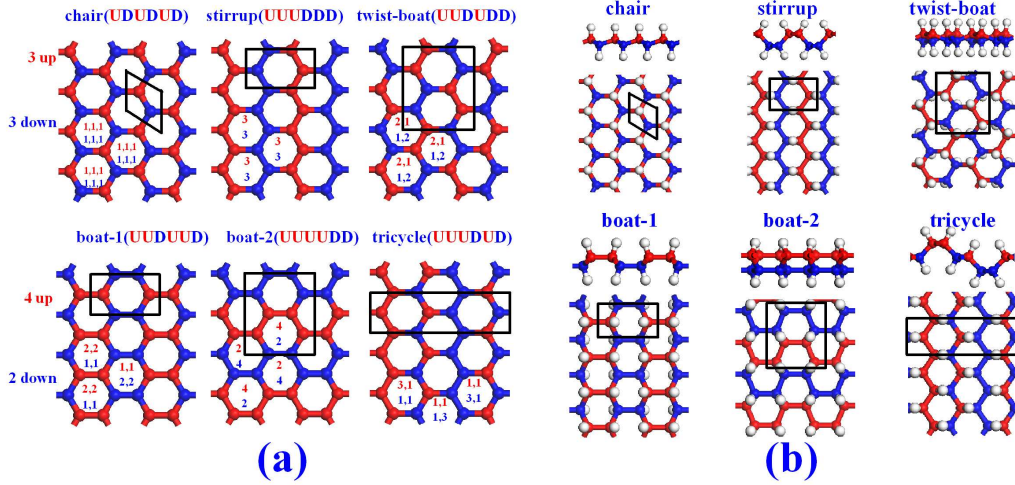


FIG. 1: (a) Schematic diagram of six possible configurations of hydrogenated graphene with equivalent hexagonal hydrocarbon rings. (b) Crystal structures (side and top views) of graphane with chair, stirrup, twist-boat, boat-1, boat-2 and tricycle configurations, respectively. In figures, the red and blue balls correspond to carbon atoms with up and down hydrogenation, respectively, and the white balls are hydrogen atoms.

TABLE I: Structure information: space group (SG), lattice constant (LC), inequivalent atom positions (positions) for H and C atoms, C-H bond length (L_{CH}), and C-C bond length (L_{CC}) for the six fundamental allotropes of graphane

System	SG and LC	positions	L_{CH} and L_{CC}
chair	P-3m1 (164) ,	H:(0.3333, 0.6667, 0.5893)	C-H: 1.110
UDUDUD	a=b=2.504; c=15.0	C:(0.3333, 0.6667, 0.5153)	C-C: 1.537
tricycle	Pbcm (57)	H1:(0.4328, 0.1235, 0.2500)	C ₁ -H ₁ : 1.108
UUUDUD	a=15; b=7.681; c=2.544	C1:(0.4981, 0.0563, 0.2500)	C ₁ -C ₁ : 1.539; C ₁ -C ₂ : 1.541
		H2:(0.6364, 0.1190, 0.2500)	C ₂ -H ₂ : 1.109
		C2:(0.5731, 0.1934, 0.2500)	C ₂ -C ₂ : 1.540; C ₂ -C ₁ : 1.541
stirrup	Pmna (53)	H:(0.0000, 0.3983, 0.5085)	C-H: 1.105
UUUDDD	a=2.549; b=15.0; c=3.828	C:(0.0000, 0.3639, 0.4620)	C-C: 1.544
boat-1	pmmn (59)	H:(0.5000, 0.2562, 0.5922)	C-H: 1.105
UUDDUU	a=2.529; b=4.309; c=15.0	C:(0.5000, 0.1822, 0.5216)	C-C: 1.537; 1.570
boat-2	Pbcm (57)	H:(0.3987, 0.4932, 0.5036)	C-H: 1.103
UUUDDD	a=15.0; b=4.585; c=4.328	C:(0.4622, 0.5939, 0.4317)	C-C: 1.542; 1.548; 1.573
twist-boat	Pcca (54)	H:(0.1215, 0.4079, 0.5609)	C-H: 1.106
UUUDDD	a=4.417; b=15.0; c=4.987	C:(0.0904, 0.4788, 0.6154)	C-C: 1.542; 1.548; 1.562

keeping the equivalence of the hexagonal hydrocarbon rings in the systems, through re-examining the systems with 4U and 3U hydrogenations (here, 4U and 3U are identical to 2U and 3U systems, and 6U and 5U are abandoned due to their instability), we find a new hydrogenated graphene with 4up/2down configuration satisfying the equivalent requirement as in the five most stable graphane allotropes. Such graphane allotrope is named as tricycle allotrope. The hydrogenation patterns of all the five most stable graphane allotropes proposed previously and the one proposed in our present work are indicated in Fig. 1 (a). They can be divided in to two groups, namely, 3up/3down and 4up/2down. Their

corresponding crystal structures including side and top views are shown in Fig. 1 (b).

The structures, relative stability and electronic properties of these six fundamental 2D graphane allotropes are systematically investigated using first-principles methods in the framework of density functional theory (DFT). All calculations are performed within the general gradient approximation (GGA) [13] as implemented in Vienna ab initio simulation package (VASP) [14, 15]. The interactions between nucleus and the valence electrons are described by the projector augmented wave (PAW) method [16, 17]. A plane-wave basis with a cutoff energy of 500 eV is used to expand the wave

TABLE II: The calculated Cohesive energy (E_{coh} : eV/atom), Gibbs free energy (δG : meV/atom), band gap (E_g : eV), layer thickness (LT: Å) and surface work function (SWF: eV) for the six graphane allotropes.

Item	chair	tricycle	stirrup	boat-1	boat-2	twist-boat
E_{coh}	-5.222	-5.210	-5.194	-5.171	-5.155	-5.147
δG	-103	-91.2	-74.3	-51.7	-35.6	-27.8
Band gap	3.491	3.446	3.340	3.374	3.412	3.529
LT	2.679	4.093	3.053	2.758	3.039	2.761
SWF	3.916	4.528	4.407	4.416	4.457	4.543

functions. The Brillouin Zone (BZ) sample meshes are set to be dense enough (less than $0.21/\text{\AA}$) to ensure the accuracy of our calculations. Crystal lattices and atom positions of all graphane allotropes are fully optimized up to the residual force on every atom less than 0.01 eV/\AA through the conjugate-gradient algorithm.

RESULTS AND DISCUSSION

Structures

The optimized structures of chair, stirrup, boat-1, boat-2, twist-boat and tricycle graphane allotropes are shown in Fig. 1 (b) and their structural information is summarized in Tab. I. The lattice constants for chair (P-3m1) and boat-1 (Pmmn) graphane allotropes are ($a=2.504 \text{ \AA}$, $b=2.504 \text{ \AA}$, $c=15.0 \text{ \AA}$) and ($a=2.529 \text{ \AA}$, $b=4.309 \text{ \AA}$, $c=15.0 \text{ \AA}$), respectively. The lattice constants, H-H bond length and C-C bond length for chair and boat-1 graphane allotropes are in good agreement with previous report[6]. Such consistency confirms the correctness of our calculations. The lattice constants for boat-2 (Pbcm), stirrup (Pmna) and twist-boat (Pcca) graphane allotropes are ($a=15.0 \text{ \AA}$, $b=4.585 \text{ \AA}$, $c=4.328 \text{ \AA}$), ($a=2.549 \text{ \AA}$, $b=15.0 \text{ \AA}$, $c=3.828 \text{ \AA}$), and ($a=4.585 \text{ \AA}$, $b=15.0 \text{ \AA}$, $c=4.328 \text{ \AA}$), respectively. All these five graphane allotropes have only one inequivalent CH pair in their crystal cell. The inequivalent H and C atom positions can be found in Tab. I and elsewhere [6, 10, 12]. The tricycle graphane allotrope proposed in present work contains two pairs of inequivalent CH. However, similar to the previously proposed allotropes, it contains only one inequivalent six-carbon ring. Tricycle graphane belongs to Pbcm space group and its lattice constants are $a=15.0 \text{ \AA}$, $b=7.681 \text{ \AA}$ and $c=2.544 \text{ \AA}$. Four inequivalent atoms in the unit cell of tricycle graphane locate at positions of (0.4328, 0.1235, 0.2500), (0.4981, 0.0563, 0.2500), (0.6364, 0.1190, 0.2500) and (0.5731, 0.1934, 0.2500) for H1, C1, H2 and C2, respectively. The calculated bond lengths are 1.108 \AA , 1.539 \AA , 1.5109 \AA , 1.540 \AA and 1.541 \AA for $C_1\text{-H}_1$, $C_1\text{-C}_1$, $C_2\text{-H}_2$, $C_2\text{-C}_2$

and $C_1\text{-C}_2$, respectively. Its bond lengths are very close to those in chair, boat-1, boat-2, stirrup and twist-boat allotropes. The layer thicknesses of these six allotropes are summarized in Tab. II. We can see that the most thinnest is chair allotrope with a thickness of 2.6779 \AA and the thickest tricycle allotrope holds thickness of 4.093 \AA . The large thickness of tricycle graphane provides a possible way to identify its existence in experiments. Surface work function provides another way to identify these potential graphane allotropes. From Tab. II, we can see that the work function of the chair graphane is 3.916 eV , which is the smallest. The work functions for other four graphane allotropes of tricycle, stirrup, boat-1, boat-2 and twist-boat are 4.528 eV , 4.407 eV , 4.416 eV , 4.457 eV and 4.543 eV , respectively. one can identify these allotropes through the values of their surface work functions in field emission experiments.

Stability

The relative stability of these allotropes can be evaluated through comparing their cohesive energy per atom (E_{coh}). Low energy usually means high probability to be discovered in the same experimental condition. To evaluate the thermodynamic stability of these new allotropes of graphane, the Gibbs free energy (δG) is calculated according to $\delta G = E_{coh} - x_H \mu_H - x_C \mu_C$, where E_{tot} is the cohesive energy per atom of the graphanes with different compositions, x_i means the molar fraction of atom i ($i=H, C$) in the structure with $x_H + x_C = 1$, and μ_i is the chemical potential of each constituent atom. The μ_H is chosen as the binding energy per atom of the H_2 molecular and μ_C is the cohesive energy per atom of a single graphane. The calculated cohesive energies and Gibbs free energies for all graphane allotropes are listed in Tab. II. We can see that the most stable one is chair graphane. Its negative δG of -103 meV/atom indicates high probability to be synthesized from graphene and H_2 . The tricycle graphane proposed is the second stable graphane allotrope with only 12 meV/atom of δG above the most stable chair one, indicating that it may be produced in the process of graphene hydrogenation. It is amazing that this new allotrope with $4\text{up}/2\text{down}$ configuration is more stable than the stirrup one with $3\text{up}/3\text{down}$ configuration, which is contrary to the intuitive knowledge that balanced up and down hydrogenation configuration is more stable than that of unbalanced one, (for example, chair and stirrup with $3\text{up}/3\text{down}$ hydrogenation are more stable than boat-1 and boat-2 with $4\text{up}/2\text{down}$ hydrogenation). Stirrup graphane with UUDDDD hydrogenation of $3\text{up}/3\text{down}$ is now the third stable conformer holding about 28 meV/atom of δG larger than that of the chair one. The value of δG s for stirrup, boat-1 and boat-

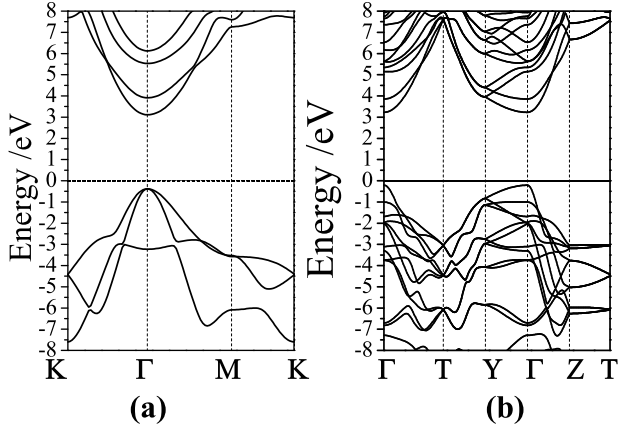


FIG. 2: Band structures of chair graphane (a) and tricycle graphane (b).

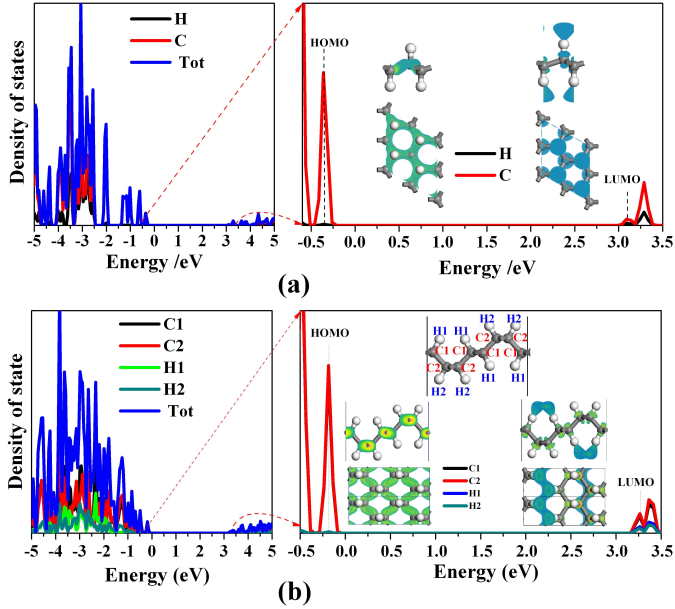


FIG. 3: Density of states for chair graphane (a) and tricycle graphane (b). Insets show the charge density distributions of to HOMO and LUMO states.

2 are -74 meV/atom, -52 meV/atom and -36 meV/atom, respectively. The negative δG s indicate that all of them may be produced in the process of graphene hydrogenation. The least stable graphane allotrope studied in our present work is the twist-boat one with UUDD hydrogenation holding energy about 80 meV/atom larger than that of the chair one. However, its negative δG of -28 meV/atom indicates that it can also be produced through the hydrogenation process from H_2 and graphene.

Electronic properties

Hydrogenation converts the hybridization of carbon atoms in graphene from sp^2 to sp^3 , inducing separation between the valence band and conduction band of graphene. All graphane allotropes with full coverage of hydrogen are direct-band-gap semiconductors with band gaps distributing in the range from 3.37 eV to 3.53 eV. The calculated band structures for the most stable chair graphane and the second stable tricycle graphane are shown in Fig. 2 (a) and (b), respectively. It is clear that the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) in these two stable hydrocarbon systems are located at Gama point. The band gaps are 3.491 eV and 3.446 eV for chair and tricycle graphanes, respectively. In Fig. 3, we show the local density of state of each inequivalent atom for chair and tricycle graphanes in (a) and (b), respectively. The right panel of Fig. 3 is the local density of states within the energy widows of (-0.5 eV, 3.5 eV) and the charge density distributions of the HOMO and the LUMO states for both systems are also shown in the figure. From 3 (a) we can see that the HOMO states of chair graphane are mainly from p_z states of carbon atoms and the corresponding charge densities mainly distribute along the C-C bonds. Its LUMO states are from both the p_z states of carbon atoms and the s states of hydrogen atoms and the corresponding charge densities mainly distribute along the C-H bonds and the weak H-H bonds. For the tricycle graphane, its LUMO states are mainly contributed by the p_z states of C_1 and C_2 atoms and the s states of H_1 and H_2 atoms and the corresponding charge densities mainly distributed along the C_1 - H_1 and C_2 - H_2 bonds and the weak H_1 - H_1 bonds. HOMO states of tricycle graphane are mainly from the p_z states of carbon atoms as shown in Fig. 3 and the corresponding charge densities mainly distribute on the C_1 - C_1 bonds and the C_2 - C_2 bonds in the two inequivalent C_1 zigzag-chain and C_2 zigzag-chains, respectively, and are absent on the inter-chains C_1 - C_2 bonds.

CONCLUSION

In summary, using first-principle calculations within the frame work of density functional theory, a tricycle graphane allotrope was proposed as the sixth fundamental graphane allotropes with a UUUDUD hydrogenation configuration satisfying the requirement of keeping each hexagonal hydrocarbon ring equivalent. Our calculations indicate that tricycle graphane is the second stable one in the graphane allotropes family proposed so far. Its negative Gibbs free energy indicates its high probability to be produced in the process of graphene hydrogenation.

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